



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|---|-----------|---|
| (51) International Patent Classification ⁵ : B08B 7/00, C23G 5/00 | A1 | (11) International Publication Number: WO 90/06189 (43) International Publication Date: 14 June 1990 (14.06.90) |
| (21) International Application Number: PCT/US89/04674 (22) International Filing Date: 23 October 1989 (23.10.89) (30) Priority data: 282,072 7 December 1988 (07.12.88) US (71) Applicant: HUGHES AIRCRAFT COMPANY [US/US]; 7200 Hughes Terrace, Los Angeles, CA 90045-0066 (US). (72) Inventors: JACKSON, David, P. ; 22328 W. Barcotta Drive, Saugus, CA 91350 (US). BUCK, Orval, F. ; 2435 25th Street, Santa Monica, CA 90405 (US). (74) Agents: LACHMAN, Mary, E. et al.; Hughes Aircraft Company, P.O. Box 45066, Bldg. C1, M.S. A126, Los Angeles, CA 90045-0066 (US). | | (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), NO, SE (European patent). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| (54) Title: CLEANING PROCESS USING PHASE SHIFTING OF DENSE PHASE GASES (57) Abstract A process for removing two or more contaminants from a substrate in a single process. The substrate to be cleaned is contacted with a dense phase gas at or above the critical pressure thereof. The phase of the dense phase gas is then shifted between the liquid state and the supercritical state by varying the temperature of the dense fluid in a series of steps between temperatures above and below the critical temperature of the dense fluid. After completion of each step in the temperature change, the temperature is maintained for a predetermined period of time in order to allow contact with the substrate and contaminants and removal of the contaminants. At each step in the temperature change, the dense phase gas possesses different cohesive energy density or solubility properties. Thus, this phase shifting of the dense fluid provides removal of a variety of contaminants from the substrate without the necessity of utilizing different solvents. In alternative embodiments, ultraviolet radiation, ultrasonic energy, or reactive dense phase gas or additives may additionally be used. | | |

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | |
|----|------------------------------|----|--|----|--------------------------|
| AT | Austria | ES | Spain | MG | Madagascar |
| AU | Australia | FI | Finland | ML | Mali |
| BB | Barbados | FR | France | MR | Mauritania |
| BE | Belgium | GA | Gabon | MW | Malawi |
| BF | Burkina Faso | GB | United Kingdom | NL | Netherlands |
| BG | Bulgaria | HU | Hungary | NO | Norway |
| BJ | Benin | IT | Italy | RO | Romania |
| BR | Brazil | JP | Japan | SD | Sudan |
| CA | Canada | KP | Democratic People's Republic of Korea | SE | Sweden |
| CF | Central African Republic | KR | Republic of Korea | SN | Senegal |
| CG | Congo | LI | Liechtenstein | SU | Soviet Union |
| CH | Switzerland | LK | Sri Lanka | TD | Chad |
| CM | Cameroon | LU | Luxembourg | TG | Togo |
| DE | Germany, Federal Republic of | MC | Monaco | US | United States of America |
| DK | Denmark | | | | |

CLEANING PROCESS
USING PHASE SHIFTING OF
DENSE PHASE GASES

1

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates generally to the use of
dense phase gases for cleaning substrates. More
particularly, the present invention relates to a process
utilizing phase shifting of dense phase gases or gas
10 mixtures in order to enhance the cleaning of a wide
variety of substrates, including complex materials and
hardware.

2. Description of Related Art

15 Conventional solvent-aided cleaning processes are
currently being re-evaluated due to problems with air
pollution and ozone depletion. In addition, recent
environmental legislation mandates that many of the
organic solvents used in these processes be banned or
their use severely limited. The use of dense phase gases
20 or gas mixtures for cleaning a wide variety of materials
has been under investigation as an alternative to the
above-mentioned solvent-based cleaning processes. A dense
phase gas is a gas compressed to either supercritical or
subcritical conditions to achieve liquid-like densities.
25 These dense phase gases or gas mixtures are also referred

1 to as dense fluids. Unlike organic solvents, such as
n-hexane or 1,1,1-trichloroethane, dense fluids exhibit
unique physical and chemical properties such as low
surface tension, low viscosity, and variable solute
5 carrying capacity.

The solvent properties of compressed gases is well
known. In the late 1800's, Hannay and Hogarth found that
inorganic salts could be dissolved in supercritical
ethanol and ether (J. B. Hannay and H. Hogarth,
10 J.Proc.Roy.Soc. (London), 29, p. 324, 1897). By the early
1900's, Buchner discovered that the solubility of organics
such as naphthalene and phenols in supercritical carbon
dioxide increased with pressure (E. A. Buchner,
Z.Physik.Chem., 54, p. 665, 1906). Within forty years
15 Francis had established a large solubility database for
liquified carbon dioxide which showed that many organic
compounds were completely miscible (A. W. Francis,
J.Phys.Chem., 58, p. 1099, 1954).

In the 1960's there was much research and use of dense
20 phase gases in the area of chromatography. Supercritical
fluids (SCF) were used as the mobile phase in separating
non-volatile chemicals (S. R. Springston and M. Novotny,
"Kinetic Optimization of Capillary Super-critical
Chromatography using Carbon Dioxide as the Mobile Phase",
25 CHROMATOGRAPHIA, Vol. 14, No. 12, p. 679, December 1981).
Today the environmental risks and costs associated with
conventional solvent-aided separation processes require
industry to develop safer and more cost-effective
alternatives. The volume of current literature on
30 solvent-aided separation processes using dense carbon
dioxide as a solvent is evidence of the extent of
industrial research and development in the field.
Documented industrial applications utilizing dense fluids
include extraction of oil from soybeans (J. P. Friedrich
35 and G. R. List and A. J. Heakin, "Petroleum-Free Extracts

1 of Oil from Soybeans", JAOCS, Vol. 59, No. 7, July 1982),
decaffination of coffee (C. Grimmett, Chem.Ind., Vol. 6,
p. 228, 1981), extraction of pyridines from coal
(T. G. Squires, et al, "Super-critical Solvents. Carbon
5 Dioxide Extraction of Retained Pyridine from Pyridine
Extracts of Coal", FUEL, Vol. 61, November 1982),
extraction of flavorants from hops (R. Vollbrecht,
"Extraction of Hops with Supercritical Carbon Dioxide",
Chemistry and Industry, 19 June 1982), and regenerating
10 absorbents (activated carbon) (M. Modell, "Process for
Regenerating Absorbents with Supercritical Fluids", United
States Patent No. 4,124,528, 7 November 1978).

Electro-optical devices, lasers and spacecraft
assemblies are fabricated from many different types of
15 materials having various internal and external geometrical
structures which are generally contaminated with more than
one type of contamination. These highly complex and
delicate assemblies can be classified together as "complex
hardware". Conventional cleaning techniques for removing
20 contamination from complex hardware require cleaning at
each stage of assembly. In addition to the above-
mentioned problems with conventional solvent-aided
cleaning techniques, there is also a problem of
recontamination of the complex hardware at any stage
25 during the assembly process. Such recontamination
requires disassembly, cleaning, and reassembly.
Accordingly, there is a present need to provide
alternative cleaning processes which are suitable for use
in removing more than one type of contamination from
30 complex hardware in a single process.

SUMMARY OF THE INVENTION

35 In accordance with the present invention, a cleaning
process is provided which is capable of removing different

1 types of contamination from a substrate in a single
process. The process is especially well-suited for
removing contaminants such as oils, grease, flux residues
and particulates from complex hardware.

5 The present invention is based on a process wherein
the substrate to be cleaned is contacted with a dense
phase gas at a pressure equal to or above the critical
pressure of the dense phase gas. The phase of the dense
10 phase gas is then shifted between the liquid state and the
supercritical state by varying the temperature of the
dense fluid in a series of steps between temperatures
above and below the critical temperature of the dense
fluid. After completion of each step in the temperature
15 change, the temperature is maintained for a predetermined
period of time in order to allow contact with the
substrate and contaminants and removal of the
contaminants. At each step in the temperature change, the
dense phase gas possesses different cohesive energy
20 density or solubility properties. Thus, this phase
shifting of the dense fluid provides removal of a variety
of contaminants from the substrate without the necessity
of utilizing different solvents.

In an alternative embodiment of the present invention,
the cleaning or decontamination process is further
25 enhanced by exposing the dense phase gas to ultraviolet
(UV) radiation during the cleaning process. The UV
radiation excites certain dense phase gas molecules to
increase their contaminant-removal capability.

In another alternative embodiment of the present
30 invention ultrasonic energy is applied during the cleaning
process. The ultrasonic energy agitates the dense phase
gas and substrate surface to provide enhanced
contamination removal.

In yet another alternative embodiment of the present
35 invention, a dense phase gas which reacts with the
contaminants is used to enhance contaminant removal.

1 The above-discussed and many other features and
attendant advantages of the present invention will become
better understood by reference to the following detailed
description when considered in conjunction with the
5 accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

10 FIG. 1 presents a phase diagram for a preferred
exemplary dense phase gas in accordance with the present
invention, and a corresponding curve of cohesive energy
versus temperature.

15 FIG. 2 is a diagram illustrating an exemplary
temperature cycling sequence used to produce the phase
shifting in accordance with the present invention.

FIG. 3 is a flowchart setting forth the steps in an
exemplary process in accordance with the present invention.

20 FIG. 4 is a diagram of an exemplary system for use in
accordance with the present invention.

FIG. 5a and FIG. 5b are schematic diagrams of
exemplary racks used to load and hold the substrates to be
cleaned in accordance with the present process.

25 FIG. 6 is a partial sectional view of a preferred
exemplary cleaning vessel for use in accordance with a
first embodiment of the present invention.

FIG. 7 is an alternate exemplary cleaning vessel in
accordance with a second embodiment of the present
invention using multi-phase dense fluid cleaning.

30 FIG. 8 is an alternative exemplary cleaning vessel in
accordance with a third embodiment of the present
invention for use in applying sonic energy during cleaning.

35 FIGS. 9a and 9b show an alternate exemplary cleaning
vessel for use in applying radiation to the dense phase
gas during the cleaning process of fourth and fifth
embodiments of the present invention.

1

DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 The dense phase fluids which may be used in accordance with the present invention include any of the known gases which may be converted to supercritical fluids or liquified at temperatures and pressures which will not degrade the physical or chemical properties of the substrate being cleaned. These gases typically include, but are not limited to: (1) hydrocarbons, such as methane, ethane, 10 propane, butane, pentane, hexane, ethylene, and propylene; (2) halogenated hydrocarbons such as tetrafluoromethane, chlorodifluoromethane, sulfur hexafluoride, and perfluoropropane; (3) inorganics such as carbon dioxide, ammonia, helium, krypton, argon, and nitrous oxide; and 15 (4) mixtures thereof. The term "dense phase gas" as used herein is intended to include mixtures of such dense phase gases. The dense phase gas selected to remove a particular contaminant is chosen to have a solubility chemistry which is similar to that of the targeted 20 contaminant. For example, if hydrogen bonding makes a significant contribution to the internal cohesive energy content, or stability, of a contaminant, the chosen dense phase gas must possess at least moderate hydrogen bonding ability in order for solvation to occur. In some cases, a 25 mixture of two or more dense phase gases may be formulated in order to have the desired solvent properties, as discussed hereinbelow with regard to an alternative embodiment of this invention. The selected dense phase gas must also be compatible with the substrate being 30 cleaned, and preferably has a low cost and high health and safety ratings.

Carbon dioxide is a preferred dense phase gas for use in practicing the present invention since it is inexpensive and non-toxic. The critical temperature of 35 carbon dioxide is 305° Kelvin (32°C) and the critical

1 pressure is 72.9 atmospheres. The phase diagram for
carbon dioxide is set forth in FIG. 1. At pressures above
the critical point, the phase of the carbon dioxide can be
5 shifted between the liquid phase and supercritical fluid
phase by varying the temperature above or below the
critical temperature of 305 Kelvin (K).

In accordance with the present invention, a single
dense phase gas or gas mixture is phase shifted in order
to provide a spectrum of solvents which are capable of
10 removing a variety of contaminants. "Phase shifting" is
used herein to mean a shift between the liquid state and
the supercritical state as represented by the bold
embodiment of this invention. The selected dense phase
arrow 10 in FIG. 1. The phase shifting is accomplished by
15 varying the temperature of the dense phase gas while
maintaining the pressure at a relatively constant level
which is at or above the critical pressure of the dense
phase gas. The pressure is predetermined by computation
to provide the necessary solvent spectrum during
20 temperature cycling, as described in greater detail
hereinbelow. The temperature of the dense phase gas is
varied in a series of steps between a temperature above
the critical temperature of the dense phase gas and a
temperature below this critical temperature. As indicated
25 in curve 12 in FIG. 1, this temperature change produces a
change in the cohesive energy density or solubility
parameter of the dense phase gas. As shown in FIG. 1,
increasing the temperature of dense phase carbon dioxide
from 300K to 320K changes the gas solvent cohesive energy
30 content from approximately 24 megapascals^{1/2} (MPa^{1/2}) to
12 MPa^{1/2}. This change in cohesive energy content produces
a change in the solvent properties of the dense phase
gas. Thus, in accordance with the present invention, the
solvent properties of the dense phase gas may be
35 controlled in order to produce a variation in solvent

1 properties such that the dense phase gas is capable of
dissolving or removing a variety of contaminants of
differing chemical composition in a single treatment
process. A spectrum of distinct solvents is provided from
5 a single dense phase gas or gas mixture. The cohesive
energy of the dense phase gas is matched to that of the
contaminant in order to remove the contaminant.
Optionally, the cohesive energy of the dense phase gas is
also matched to that of the substrate in order to produce
10 substrate swelling, as discussed in further detail below.

The phase shifting is accomplished in accordance with
the present invention by a step-wise change in
temperature, as indicated by way of example in FIG. 2,
where T is the process or operating temperature and T_c
15 is the critical temperature. In FIG. 2, at a constant
pressure greater than the critical pressure, the
temperature is incrementally decreased to a point below
 T_c and is then incrementally increased to the starting
temperature above T_c . After each step in the
20 temperature change, the temperature is held constant for a
predetermined period of time during which the substrate
and contaminants are exposed to the dense phase gas and
contaminants are removed. As discussed with regard to
FIG. 1, at each step in the temperature change of FIG. 2,
25 the dense phase gas has different solvent properties,
i.e., a different solvent exists at each step.
Consequently, a variety of contaminants can be removed by
this solvent spectrum. The stepwise change from $T > T_c$ to
 $T < T_c$ and back to $T > T_c$ is referred to herein as a
30 "temperature cycle." The starting point for the
temperature cycling maybe either above or below the
critical temperature. In accordance with the present
process, the temperature cycle may be repeated several
times, if required, in order to produce increased levels

1 of contaminant removal. Each successive cycle removes
more contaminants. For xample after one cycle, 30
percent of the contaminants may be removed; after the
second cycle, 60 percent of the contaminants may be
5 removed; and after the third cycle, 75 percent of the
contaminants may be removed. The phase shift cycle of the
present invention also improves contaminant removal by
enhancing floatation and inter-phase transfer of
contaminants, thermally-aided separation of contaminants,
10 and micro-bubble formation.

The values of operating temperature and pressure used
in practicing the process of the present invention may be
calculated as follows. First, the cohesive energy value
of the contaminants is computed or a solubility value is
15 obtained from published data. Next, based upon the
critical temperature and pressure data of the selected
dense phase gas or gas mixture, and using gas solvent
equations, such as those of Giddings, Hildebrand, and
others, a set of pressure/temperature values is computed.
20 Then, a set of curves of solubility parameter versus
temperature is generated for various pressures of the
dense phase gas. From these curves, a phase shift
temperature range at a chosen pressure can be determined
which brackets the cohesive energies (or solubility
25 parameters) of the contaminants. Due to the complexity of
these calculations and analyses, they are best
accomplished by means of a computer and associated
software.

The number of times the phase shift cycle is repeated,
30 the amount of change in temperature for each step in the
cycle, and the residence time at each step are all
dependent upon the extent of contaminant removal which is
required, and can readily be determined experimentally as
follows. The substrate is subjected to one or more phase
35 shift cycles in accordance with the present invention, and
then the substrate is examined to determine the extent of

1 cleaning which has been accomplished. The substrate may
be examined by visual or microscopic means or by testing,
such as according to the American Society for Testing and
Materials, Standard E595 "Total Mass Loss (TML) and
5 Collected Volatile Condensable Material (CVCM)."
Depending on the results obtained, selected process
parameters may be varied and their effect on the extent of
contaminant removal determined. From this data, the
optimum process parameters for the particular cleaning
10 requirements may be determined. Alternatively, the
exhausted gas solvent may be analyzed to determine the
amount of contaminants contained therein. Gravimetric,
spectroscopic, or chromatographic analysis may be used for
this purpose. The extent of contaminant removal is then
15 correlated with the various process parameters to
determine the optimum conditions to be used. Typical
process parameters which have been found to be useful
include, but are not limited to, the following: variation
of the temperature above the critical temperature by about
20 5 to 100K; variation of the temperature below the critical
temperature by about 5 to 25K; step changes in temperature
of about 5 to 10K; and residence time at each step of
about 5 to 30 minutes.

25 A flowchart showing the steps in the cleaning process
of a first embodiment of the present invention is
presented in FIG. 3. The process is carried out in a
cleaning vessel which contains the substrate to be
cleaned. Various exemplary cleaning vessels will be
described in detail below. As shown in FIG. 3, the
30 cleaning vessel is initially purged with an inert gas or
the gas or gas mixture to be used in the cleaning
process. The temperature in the pressure vessel is then
adjusted to a temperature either below the critical
temperature (subcritical) for the gas or gas mixture or
35 above or equal to the critical temperature (supercritical)

1 for the gas. The cleaning vessel is next pressurized to a
pressure which is greater than or equal to the critical
pressure for the gas or gas mixture. At this point, the
gas is in the form of a dense fluid. The phase of this
5 dense fluid is then shifted between liquid and
supercritical states, as previously described, by varying
the temperature over a predetermined range above and below
the critical point, as determined by the type and amount
of contaminants to be removed. Control of temperature,
10 pressure and gas flow rates is best accomplished under
computer control using known methods.

The process of controlled temperature variation to
achieve phase shifting has been discussed with regard to
FIG. 2. Phase shifting back and forth between the liquid
15 and supercritical states can be performed as many times as
required. After phase shifting has been completed, the
cleaning vessel is then depressurized and the treated
substrate is removed and packaged or treated further.

When cleaning substrates which will be used in the
20 space environment, the dense fluids may themselves become
contaminants when subjected to the space environment.
Therefore, substrates to be used in space are subjected to
an additional thermal vacuum degassing step after the
high-pressure dense fluid cleaning process. This step is
25 shown in FIG. 3 wherein the cleaning vessel is
depressurized to a vacuum of approximately 1 Torr
(millimeter of mercury) and a temperature of approximately
395K (250°F) is applied for a predetermined (i.e.,
precalculated) period of time in order to completely degas
30 the hardware and remove any residual gas from the
hardware. The depressurization of the cleaning vessel
after the cleaning process has been completed is carried
out at a rate determined to be safe for the physical
characteristics, such as tensile strength, of the
35 substrate.

1 For certain types of substrates, such as polymeric
materials, internal dense fluid volumes are high upon
completion of the cleaning process. Accordingly, during
depressurization, the internal interstitial gas molar
5 volume changes drastically. The gas effusion rate from
the polymer is limited depending upon a number of factors,
such as temperature, gas chemistry, molar volume, and
polymer chemistry. In order to ease internal stresses
caused by gas expansion, it is preferred that the fluid
10 environment in the cleaning vessel be changed through
dense gas displacement prior to depressurization,
maintaining relatively constant molar volume. The
displacement gas is chosen to have a diffusion rate which
is higher than that of the dense phase gas. This step of
15 dense gas displacement is shown in FIG. 3 as an optional
step when polymeric materials are being cleaned. For
example, if a non-polar dense phase cleaning fluid, such
as carbon dioxide, has been used to clean a non-polar
polymer, such as butyl rubber, then a polar fluid, such as
20 nitrous oxide, should be used to displace the non-polar
dense fluid prior to depressurization since the polar
fluid will generally diffuse more readily from the polymer
pores. Alternatively, dense phase helium may be used to
displace the dense phase gas cleaning fluid since helium
25 generally diffuses rapidly from polymers upon
depressurization.

The present invention may be used to clean a wide
variety of substrates formed of a variety of materials.
The process is especially well adapted for cleaning
30 complex hardware without requiring disassembly. Some
exemplary cleaning applications include: defluxing of
soldered connectors, cables and populated circuit boards;
removal of photoresists from substrates; decontamination
of cleaning aids such as cotton- or foam-tipped
35 applicators, wipers, gloves, etc; degreasing of complex

1 hardware; and decontamination of electro-optical, laser
and spacecraft complex hardware including pumps,
transformers, rivets, insulation, housings, lin ar
bearings, optical bench assemblies, heat pipes, switches,
5 gaskets, and active metal castings. Contaminant materials
which may be removed from substrates in accordance with
the present invention include, but are not limited to,
oil, grease, lubricants, solder flux residues,
photoresist, particulates comprising inorganic or organic
10 materials, adhesive residues, plasticizers, unreacted
monomers, dyes, or dielectric fluids. Typical substrates
from which contaminants may be removed by the present
process include, but are not limited to, substrates formed
of metal, rubber, plastic, cotton, cellulose, ceramics,
15 and other organic or inorganic compounds. The substrates
may have simple or complex configurations and may include
interstitial spaces which are difficult to clean by other
known methods. In addition, the substrate may be in the
form of particulate matter or other finely divided
20 material. The present invention has application to gross
cleaning processes such as degreasing, removal of tape
residues and functional fluid removal, and is also
especially well-adapted for precision cleaning of complex
hardware to high levels of cleanliness.

25 In accordance with an alternative embodiment of the
present invention, a mixture of dense phase gases is
formulated to have specific solvent properties. For
example, it is known that dense phase carbon dioxide does
not hydrogen bond and hence is a poor solvent for
30 hydrogen-bonding compounds, such as abietic acid, which is
a common constituent in solder fluxes. We have found by
calculation that the addition of 10 to 25 percent
anhydrous ammonia, which is a hydrogen-bonding compound,
to dry liquid carbon dioxide modifies the solvent
35 chemistry of the latter to provide for hydrogen bonding

1 without changing the total cohesion energy of the dense
fluid system significantly. The anhydrous ammonia gas is
blended with the carbon dioxide gas and compressed to
liquid-state densities, namely the subcritical or
5 supercritical state. These dense fluid blends of CO₂
and NH₃ are useful for removing polar compounds, such as
plasticizers from various substrates. In addition to
possessing hydrogen-bonding ability, the carbon
dioxide/ammonia dense fluid blend can dissolve ionic
10 compounds, and is useful for removing residual ionic flux
residues from electronic hardware and for regenerating
activated carbon and ion exchange resins. This particular
dense phase solvent blend has the added advantage that it
is environmentally acceptable and can be discharged into
15 the atmosphere. Similar blends may be made using other
non-hydrogen-bonding dense fluids, such as blends of
ammonia and nitrous oxide or ammonia and xenon.

An exemplary system for carrying out the process of
the present invention is shown diagrammatically in
20 FIG. 4. The system includes a high pressure cleaning
chamber or vessel 12. The substrate is placed in the
chamber 12 on a loading rack as shown in FIG. 5a or
FIG. 5b. The temperature within the chamber 12 is
controlled by an internal heater assembly 14 which is
25 powered by power unit 16 which is used in combination with
a cooling system (not shown) surrounding the cleaning
vessel. Coolant is introduced from a coolant reservoir 18
through coolant line 20 into a coolant jacket or other
suitable structure (not shown) surrounding the high
30 pressure vessel 12. The dense fluid used in the cleaning
process is fed from a gas reservoir 22 into the chamber 12
through pressure pump 24 and inlet line 25. The system
may be operated for batch-type cleaning or continuous
cleaning. For batch-type cleaning, the chamber 12 is
35 pressurized to the desired level and the temperature of

1 the dense phase gas is adjusted to the starting point for
the phase shifting sequence, which is either above or
below the critical temperature of the dense phase gas.
The vessel is repeatedly pressurized and depressurized
5 from the original pressure starting point to a pressure
below the critical pressure. Sequentially, the
temperature of the vessel is adjusted up or down,
depending on the types of contaminants, and the
pressurization/depressurization steps are carried out.
10 The resulting dense fluid containing contaminants is
removed from the chamber 12 through exhaust line 26. The
cleaning vessel may be repressurized with dense phase gas
and depressurized as many times as required at each
temperature change. The exhaust line may be connected to
15 a separator 28 which removes the entrained contaminants
from the exhaust gas thereby allowing recycling of the
dense phase gas. Phase shifting by temperature cycling is
continued and the above-described depressurization and
repressurizations are performed as required to achieve the
20 desired level of cleanliness of the substrate.

For continuous cleaning processes, the dense fluid is
introduced into chamber 12 by pump 24 at the same rate
that contaminated gas is removed through line 26 in order
to maintain the pressure in chamber 12 at or above the
25 critical pressure. This type of process provides
continual removal of contaminated gas while the phase of
the dense fluid within chamber 12 is being shifted back
and forth between liquid and supercritical states through
temperature cycling.

30 The operation of the exemplary system shown
schematically in FIG. 4 is controlled by a computer 30
which utilizes menu-driven advanced process development
and control (APDC) software. The analog input, such as
temperature and pressure of the chamber 12, is received by
35 the computer 30 as represented by arrow 32. The computer

1 provides digital output, as represented by arrow 33 to
control the various valves, internal heating and cooling
systems in order to maintain the desired pressure and
5 temperature within the chamber 12. The various programs
for the computer will vary depending upon the chemical
composition and geometric configuration of the particular
substrate being cleaned, the contaminant(s) being removed,
the particular dense fluid cleaning gas or gas mixture,
10 and the cleaning times needed to produce the required
end-product cleanliness. Normal cleaning times are on the
order of four hours or less.

Referring to FIGS. 3 and 4, an exemplary cleaning
process involves initially placing the hardware into the
cleaning vessel, chamber 12. The chamber 12 is closed and
15 purged with clean, dry inert gas or the cleaning gas from
reservoir 22. The temperature of the chamber 12 is then
adjusted utilizing the internal heating element 14 and
coolant from reservoir 18 to which is provided externally
through a jacketing system, in order to provide a
20 temperature either above or below the critical temperature
for the cleaning gas or gas mixtures. The chamber 12 is
then pressurized utilizing pump 24 to a pressure equal to
or above the critical pressure for the particular dense
phase gas cleaning fluid. This critical pressure is
25 generally between about 20 atmospheres (300 pounds per
square inch or 20.6 kilograms per square centimeter) and
102 atmospheres (1500 pounds per square inch or 105.4
kilograms per square centimeter). The processing pressure
is preferably between 1 and 272 atmospheres (15 and 4000
30 pounds per square inch or 1.03 and 281.04 kilograms per
square centimeter) above the critical pressure, depending
on the breadth of solvent spectrum and associated phase
shifting range which are required.

Once the pressure in chamber 12 reaches the desired
35 point above the critical pressure, the pump 24 may be

1 continually operated and exhaust line 26 opened to provide
continuous flow of dense fluid through the chamber 12
while maintaining constant pressure. Alternatively, the
exhaust line 26 may be opened after a sufficient amount of
5 time at a constant pressure drop to remove contaminants,
in order to provide for batch processing. For example, a
pressure drop of 272 atmospheres (4,000 psi) to 102
atmospheres (1500 psi) over a 20-minute cleaning period
can be achieved.

10 Phase shifting of the dense fluid between liquid and
supercritical states is carried out during the cleaning
process. This phase shifting is achieved by controlled
ramping of the temperature of the chamber 12 between
temperatures above the critical temperature of the dense
15 fluid and temperatures below the critical temperature of
the dense fluid while maintaining the pressure at or above
the critical pressure for the dense fluid. When carbon
dioxide is used as the dense fluid, the temperature of
chamber 12 is cycled above and below 305K (32° centigrade).

20 FIG. 5 shows two exemplary racks which may be used to
load and hold the substrates to be cleaned in accordance
with the present invention. FIG. 5a shows a vertical
configuration, while FIG. 5b shows a horizontal
configuration. In FIGS. 5a and 5b, the following elements
25 are the same as those shown in FIG. 4: chamber or
pressure vessel 12, gas inlet line 25, and gas outlet
line(s) 26. A rack 13 with shelves 15 is provided to hold
the substrates 17 to be treated in accordance with the
present process. The rack 13 and shelves 15 are made of a
30 material which is chemically compatible with the dense
fluids used and sufficiently strong to withstand the
pressures necessary to carry out the present process.
Preferred materials for the rack and shelves are stainless
steel or teflon. The shelves 15 are constructed with
35 perforations or may be mesh in order to insure the

1 unobstructed flow of the dense fluid and h at transfer
around the substrates. The rack 13 may have any
convenient shape, such as cylindrical or rectangular, and
is configured to be compatible with the particular
5 pressure vessel used. The vertical configuration of
FIG. 5a is useful with a pressure vessel of the type shown
in FIG. 6 or 7 herein, whereas the horizontal
configuration of FIG. 5b is useful with a pressure vessel
of the type shown in FIG. 8 herein. As shown in FIG. 5a,
10 legs or "stand-offs" 21 are provided in order to elevate
the rack above the sparger carrying the dense phase gas.
As indicated in FIG. 5b, the rack is held on stand-offs
(not shown) so that it is located in the upper half of the
chamber in order to prevent obstruction of fluid flow.
15 Optionally, in both of the configurations of FIGS. 5a
and 5b, an additive reservoir 19 may be used in order to
provide a means of modifying the dense phase gas by
addition of a selected material, such as methanol or
hydrogen peroxide. The reservoir 19 comprises a shallow
20 rectangular or cylindrical tank. The modifier is placed
in the reservoir 19 when the substrate is loaded into the
chamber 12. The modifier may be a free-standing liquid or
it may be contained in a sponge-like absorbent material to
provide more controlled release. Vapors of the modifier
25 are released from the liquid into the remainder of the
chamber 12 during operation of the system. The modifier
is chosen to enhance or change certain chemical properties
of the dense phase gas. For example, the addition of
anhydrous ammonia to xenon provides a mixture that
30 exhibits hydrogen bonding chemistry, which xenon alone
does not. Similarly, the modifier may be used to provide
oxidizing capability or reducing capability in the dense
phase gas, using liquid modifiers such as ethyl alcohol,
water, acid, base, or peroxide.

1 An exemplary high pressure cleaning vessel for use in
practicing a first embodiment of the present process is
shown at 40 FIG. 6. The vessel or container 40 is
suitable for use as the high pressure cleaning vessel
5 shown at 12 in the system depicted in FIG 4. The high
pressure cleaning vessel 40 includes a cylindrical outer
shell 42 which is closed at one end with a removable
enclosure 44. The shell 42 and enclosure 44 are made from
conventional materials which are chemically compatible
10 with the dense fluids used and sufficiently strong to
withstand the pressures necessary to carry out the
process, such as stainless steel or aluminum. The
removable enclosure 44 is provided so that materials can
be easily placed into and removed from the cleaning
15 zone 46 within outer shell 42.

An internal heating element 48 is provided for
temperature control in combination with an external
cooling jacket 59 surrounding the shell 42. Temperature
measurements to provide analog input into the computer for
20 temperature control are provided by thermocouple 50. The
gas solvent is fed into the cleaning zone 46 through inlet
52 which is connected to sparger 54. Removal of gas or
dense fluid from the cleaning zone 46 is accomplished
through exhaust ports 56 and 58.

25 The cleaning vessel 40 is connected into the system
shown in FIG. 4 by connecting inlet 52 to inlet line 25,
connecting heating element 48 to power source 16 using
power leads 49, and connecting exhaust outlets 56 and 58
to the outlet line 26. The thermocouple 50 is connected
30 to the computer 30.

In accordance with a second embodiment of the present
invention, the contaminated substrate to be cleaned is
suspended in a liquid suspension medium, such as deionized
water, while it is subjected to the phase shifting of the
35 dense phase gas as previously described. FIG. 7 shows an

1 exemplary cleaning vessel which may be used to practice
this embodiment of the present invention. The system
shown in FIG. 7 is operated in the same manner as the
system shown in FIG. 6 with the exceptions noted below.
5 In FIG. 7, the following elements are the same as those
described in previous figures: chamber or cleaning
vessel 12, substrate 17, gas inlet line 25, and gas
exhaust line 26. Within the chamber 12, there is an inner
container 41, which is formed of a chemically resistant
10 and pressure resistant material, such as stainless steel.
The container 41 holds the liquid 43, in which the
substrate 17 is suspended by being placed on a rack (not
shown). A gas sparger 45 is provided for introducing the
dense phase gas through the inlet line 25 into the lower
15 portion of the container 41 and into the liquid 43. The
phase shifting process is performed as previously
described herein, and a multiphase cleaning system is
produced. For example, if deionized water is used as the
liquid suspension medium and carbon dioxide is used as the
20 dense phase gas at a temperature greater than 305K and a
pressure greater than 70 atmospheres, the following
multiple phases result: (a) supercritical carbon dioxide,
which removes organic contaminants; (b) deionized water,
which removes inorganic contaminants; and (c) carbonic
25 acid formed in situ, which removes inorganic ionic
contaminants. In addition, during the depressurization
step as previously described herein, the gas-saturated
water produces expanding bubbles within the interstices of
the substrate as well as on the external surfaces of the
30 substrate. These bubbles aid in dislodging particulate
contaminants and in "floating" the contaminants away from
the substrate. The wet supercritical carbon dioxide
containing the contaminants passes by interphase mass
transfer from inner container 41 to chamber 12, from which
35 it is removed through exhaust line 26.

1 After the substrate 17 has been cleaned, it is rinsed
with clean hot deionized water to remove residual
contaminants, and is then vacuum dried in an oven at 350K
for 2 to 4 hours and packaged. Optionally, the substrate
5 may be first dried with alcohol prior to oven drying.

Other dense phase gases which are suitable for use in
this second embodiment of the present invention include,
but are not limited to, xenon and nitrous oxide. In
addition, the liquid suspension medium may alternatively
10 contain additives, such as surfactants or ozone, which
enhance the cleaning process. This embodiment of the
present invention is particularly well suited for
precision cleaning of wipers, gloves, cotton-tipped wooden
applicators, and fabrics.

15 In a third embodiment of the present invention, the
cleaning action of the dense fluid during phase shifting
from the liquid to supercritical states may be enhanced by
applying ultrasonic energy to the cleaning zone. A
suitable high-pressure cleaning vessel and sonifier are
20 shown at 60 in FIG. 8. The sonifier 60 includes a
cylindrical container 62 having removable enclosure 64 at
one end and ultrasonic transducer 66 at the other end.
The transducer 66 is connected to a suitable power source
by way of power leads 68. Such transducers are
25 commercially available, for example from Delta Sonics of
Los Angeles, California. Gas solvent feed line 70 is
provided for introduction of the dense fluid solvent into
the cleaning zone 74. Exhaust line 72 is provided for
removal of contaminated dense fluid.

30 The sonifier 60 is operated in the same manner as the
cleaning vessel shown in FIG. 6 except that a sparger is
not used to introduce the dense fluid into the cleaning
vessel and the temperature control of the sonification
chamber 74 is provided externally as opposed to the
35 cleaning vessel shown in FIG. 6 which utilizes an internal

1 heating element. The frequency of sonic energy applied to
the dense fluid during phase shifting in accordance with
the present invention may be within the range of about 20
5 and 80 kilohertz. The frequency may be held constant or,
preferably, may be shifted back and forth over the range
of 20 to 80 kilohertz. The use of ultrasonic energy
(sonification) increases cleaning power by aiding in
dissolving and/or suspending bulky contaminants, such as
waxes, monomers and oils, in the dense fluid.

10 Furthermore, operation of the sonic cleaner with high
frequency sonic bursts agitates the dense phase gas and
the substrate to promote the breaking of bonds between the
contaminants and the substrate being cleaned. Use of
sonification in combination with phase shifting has the
15 added advantage that the sonification tends to keep the
chamber walls clean and assists in removal of extracted
contaminants.

In accordance with a fourth embodiment of the present
invention, enhancement of the cleaning action of the dense
20 fluid may be provided by exposing the fluid to high energy
radiation. The radiation excites certain dense phase gas
molecules to increase their contaminant-removal
capability. Such gases include, but are not limited to
carbon dioxide and oxygen. In addition, radiation within
25 the range of 185 to 300 nm promotes the cleavage of
carbon-to-carbon bonds. Thus, organic contaminants are
photo-decomposed to water, carbon dioxide, and nitrogen.
These decomposition products are then removed by the dense
phase gas.

30 An exemplary cleaning vessel for carrying out such
radiation-enhanced cleaning is shown at 80 in FIG. 9. The
cleaning vessel 80 includes a container 82 which has a
removable container cover 84, gas solvent feed port 86
which has an angled bore to provide for enhanced mixing in
35 the chamber, and solvent exhaust port 88. The interior

1 surface 90 preferably includes a radiation-reflecting
liner. The preferred high energy radiation is ultraviolet
(UV) radiation. The radiation is generated from a
conventional mercury arc lamp 92, generally in the range
5 between 180 and 350 nanometers. Xenon flash lamps are
also suitable. Operation of the lamp may be either high
energy burst pulsed or continuous. A high pressure quartz
window 94, which extends deep into the chamber to achieve
a light piping effect, is provided in the container cover
10 84 through which radiation is directed into the cleaning
chamber 96. The cleaning vessel 80 is operated in the
same manner as the cleaning vessels shown in FIGS. 6 and
8. Temperature control within the cleaning chamber 96 is
provided by an external heating element and cooling jacket
15 (not shown).

The cleaning vessels shown in FIGS. 6-9 are exemplary
only and other possible cleaning vessel configurations may
be used in order to carry out the process of the present
invention. For example, cleaning vessels may be used
20 wherein both sonification and ultraviolet radiation
features are incorporated into the vessel. Furthermore, a
wide variety of external and internal heating and cooling
elements may be utilized in order to provide the necessary
temperature control to accomplish phase shifting of the
25 dense fluid between the liquid and supercritical fluid
states.

The cleaning vessel shown in FIG. 6 is especially
useful in creating temperature gradients within the
cleaning zone 46. The internally located heating element
30 48 in combination with an externally mounted cooling
jacket or chamber makes it possible to create a
temperature gradient within the cleaning chamber 46 when
the flow rate and pressure of dense fluid is constant.
Such a thermal gradient in which the temperature of the
35 dense fluid decreases moving from the center toward the

1 container walls, provides thermal diffusion of certain
contaminants away from the substrate which is usually
located centrally within the chamber. This thermal
gradient also provides "solvent zones", that is a range of
5 distinct solvents favoring certain contaminants or
contaminant groups, which enhances the contaminant removal
process.

In accordance with a fifth embodiment of the present
invention, the dense fluid may comprise a mixture of a
10 first dense phase fluid which chemically reacts with the
contaminant to thereby facilitate removal of the
contaminant, and a second dense phase fluid which serves
as a carrier for the first dense phase fluid. For
example, supercritical ozone or "superozone" is a highly
15 reactive supercritical fluid/oxidant at temperatures
greater than or equal to 270K and pressures greater than
or equal to 70 atmospheres. The ozone may be generated
external to the cleaning vessel, such as that shown in
FIG. 6, mixed with a carrier gas, and introduced into the
20 cleaning zone 46 through inlet 52. Known methods of
forming ozone from oxygen by silent direct current
discharge in air, water, or liquid oxygen and ultraviolet
light exposure of air, as described, for example, in the
publication entitled "UV/Ozone Cleaning for Organics
25 Removal on Silicon Wafers," by L. Zaronte and R. Chiu,
Paper No. 470-19, SPIE 1984 Microlithography Conference,
March 1984, Santa Clara, California; and in the
publication entitled "Investigation into the Chemistry of
the UV-Ozone Purification Process," U.S. Department of
30 Commerce, National Science Foundation, Washington D.C.,
January 1979 may be used. Optionally, the ozone may be
generated in situ within a cleaning vessel of the type
shown in FIG. 9 in which the quartz window 94 is replaced
with a quartz light pipe array which pipes the ozone-

1 producing ultraviolet light deep into the dense phase gas
mixture. Oxygen, optionally blended with a carrier gas
such as carbon dioxide, xenon, argon, krypton, or ammonia,
is introduced into chamber 80 through gas solvent feed
5 port 86. If no carrier gas is used in the input gas,
excess oxygen serves as the carrier for the newly formed
ozone. In practice, the substrate is placed in the
chamber 80 and the system is operated as described for the
system of FIG. 9. The mercury lamps 92 are activated to
10 produce 185 nanometer radiation which strikes the oxygen
gas (O_2) and converts it to ozone (O_3). After
adjustment of the system pressure and temperature to form
a dense phase gas, the superozone is transported to the
substrate surface as a dense phase gas oxidant in the
15 secondary dense fluid (i.e., dense phase carbon dioxide,
argon, oxygen, or krypton).

Superozone has both gas-like and liquid-like chemical
and physical properties, which produces increased
permeation of this dense phase gas into porous structures
or organic solids and films and more effective contaminant
20 removal. In addition, superozone is both a polar solvent
and an oxidant under supercritical conditions and
consequently is able to dissolve into organic surface
films or bulky compounds and oxidatively destroy them.
25 Oxidation by-products and solubilized contaminants are
carried away during depressurization operations previously
described. The use of superozone has the added advantage
that no hazardous by-products or waste are generated.
This embodiment of the present invention using superozone
30 is particularly useful for deep sterilization of various
materials, destroying unreacted compounds from
elastomeric/resinous materials, in-situ destruction of
organic hazardous wastes, precision cleaning of optical
surfaces; preparation of surfaces for bonding processes;

1 surface/subsurface etching of substrate surfaces, and
reducing volatile organic compound levels in substrates,
to produce materials and structures which meet NASA
requirements for space applications.

5 Other materials which chemically react with the target
contaminants may alternatively be used in this third
embodiment of the present invention. For example,
hydrogen peroxide can be used in place of ozone to provide
an oxidant to react with the target contaminants.

10 Moreover, other types or reactions besides oxidation can
be effected in accordance with the present invention. For
example, a material, such as ammonia, which can be
photodissociated to form hydrogen species, can chemically
reduce the target contaminants. A material, such as
15 fluorine gas, which can be photodissociated to form
fluorine, or other halogen radicals, can react with target
contaminants.

Examples of practice of the present invention are as
follows.

20

EXAMPLE 1

This example illustrates the use of one embodiment of
the present invention to remove a variety of contaminants
25 from a cotton-tipped wooden applicator in preparation for
using the applicator as a precision cleaning aid. The
contaminants comprised wood oils, adhesive residues,
particulate matter, cellulose, lignin, triglycerides,
resins and gums with which the applicator had become
30 contaminated during manufacture or through prior use in
precision cleaning, or by their natural composition.

The dense phase gas used in practising the present
process comprised 90 percent by volume carbon dioxide and
10 percent by volume nitrous oxide. The critical
35 temperature for carbon dioxide is approximately 305K and

1 the critical pressure is approximately 72 atmospheres.
The critical temperature of nitrous oxide is 309K and the
critical pressure is approximately 72 atmospheres.

5 The flowchart of FIG. 3 and the cleaning vessel of
FIG. 6 were used as previously described herein. The
contaminated substrate, namely the cotton-tipped wooden
applicator, was placed on a rack and then in the cleaning
vessel 12, and the vessel was purged with inert gas. The
temperature of the vessel was adjusted to approximately
10 320K. Next, the cleaning chamber was pressurized with the
carbon dioxide-nitrous oxide mixture to about
275 atmospheres. One cycle of phase shifting was carried
out by incrementally varying (ramping) the temperature of
the gas mixture from 320K to approximately 300K, which
15 changed the gas solvent cohesive energy from approximately
 $12 \text{ MPa}^{1/2}$ to $22 \text{ MPa}^{1/2}$ and then incrementally increasing
the temperature from 300K to 320K, which changed the gas
solvent cohesive energy content from approximately $22 \text{ MPa}^{1/2}$
to $12 \text{ MPa}^{1/2}$. The gas mixture was allowed to contact the
20 contaminated substrate after each temperature change
(change in solvency) for 1 to 3 minutes prior to beginning
batch or continuous cleaning operations. Phase shifting
was carried out for approximately 30 minutes at a rate of
1 cycle every 5 minutes for continuous cleaning operations,
25 and optionally for approximately 60 minutes at a rate of
1 cycle every 15 minutes for batch cleaning operations.
The cleaned substrate typically exhibited a weight loss of
2 to 4%, and solvent leachate tests showed less than
1 milligram of extractable residue per applicator. The
30 cleaned substrate was packaged and sealed.

As previously discussed, this phase shifting process
creates a "solvent spectrum" which overlaps the cohesive
energy ranges for the contaminants and therefore provides
a suitable solvent for each of the contaminants present in
35 the cotton-tipped wooden applicator.

1 The above-described procedure utilizing carbon dioxide
and nitrous oxide as the dense phase gas can be extended
to other types of substrates containing a wide range of
contaminants, including foam-tipped plastic applicators,
5 wiping cloths, cotton balls and gloves.

EXAMPLE 2

10 This example illustrates the use of the process of the
present invention in order to clean a substrate to meet
NASA outgassing requirements. The substrate comprised
soldered pin connectors and the contaminants were solder
flux residues, particulate matter, skin, oils,
plasticizers, and potential outgassing contaminants.

15 The general procedure described in Example 1 was
followed except that 100 percent carbon dioxide was used
as the dense phase gas. The phase shift temperature range
was approximately 310K to 298K at a pressure of
approximately 200 atmospheres. Phase shifting was carried
20 out for approximately 30 minutes at a rate of 1 cycle
every 10 minutes. Following gas solvent cleaning, the
vessel temperature was raised to 395K (250°F) and a
vacuum of 1 Torr was applied for 1 hour to remove residual
gas. The cleaned substrate exhibited no signs of visible
25 contamination in the pin sockets, and standard
thermal-vacuum outgassing tests in accordance with ASTM
Standard E595 showed a total mass loss (TML) of less than
1.0% and a volatile condensable material (VCM) content of
less than 0.1% for the entire assembly, which meets NASA
30 outgassing requirements. The cleaned substrate was
packaged and sealed as usual for subsequent operations.

1

EXAMPLE 3

5 The example illustrates the use of the process of the present invention to remove unreacted oils, colorants and fillers from fluorosilicone interfacial seals in order to improve insulation resistance (dielectric properties).

10 The general procedure described in Example 1 was followed except that 100 percent carbon dioxide was used as the dense phase gas. The phase shift temperature range was approximately 300K to 320K at a pressure of approximately 170 atmospheres. Phase shifting from the liquid state to the supercritical state was employed in order to first swell the bulk polymer (i.e., the fluorosilicone) in liquid CO₂ and then remove
15 interstitial contaminants during phase shift operations. Phase shifting was carried out for approximately 30 minutes at a rate of 1 cycle every 10 minutes. Following cleaning operations, the material was thermal-vacuum degassed and packaged. The cleaned substrates exhibited
20 weight losses of 4% to 10%, and the column to column insulation resistance was improved 15-fold.

EXAMPLE 4

25 This example illustrates the use of the process of the present invention to remove surface contaminants, including solder flux residues, finger oils, and particulate matter, from ferrite cores prior to encapsulation in order to eliminate possible high-voltage
30 interfacial dielectric breakdown.

The general procedure described in Example 1 was followed except that the dense phase gas comprised 75 percent by volume dry carbon dioxide and 25 percent by volume anhydrous ammonia. The phase shift temperature
35 range was approximately 375K to 298K at a pressure of

1 about 240 atmospheres. Ammonia has a critical pressure of
approximately 112 atmospheres and a critical temperature
of approximately 405K. During the phase shifting
operation, which was typically 1 cycle every 10 minutes
5 for 45 minutes, the substrate was bathed in a two-phase
system (supercritical carbon dioxide/liquid ammonia) at
temperatures above 305K and a binary solvent blend (liquid
carbon dioxide-ammonia) at temperatures below 305K.
Following cleaning operations, the substrate was packaged
10 and sealed. The cleaned substrate exhibited visibly clean
surfaces, and surface contamination tests showed less than
15 milligrams of ionic contaminants per square inch of
surface area.

The above-described cleaning operation utilizing dense
15 phase carbon dioxide and dense phase ammonia can be
extended to other types of substrates containing a wide
range of ionic/nonionic and organic/inorganic
contaminants, including printed wiring boards, electronic
connectors, spacecraft insulating blankets, and ceramic
20 daughter boards.

EXAMPLE 5

25 This example illustrates the use of the process of the
present invention to remove machining oils, finger oils,
and particulate matter from optical benches (active metal
casting) to meet NASA outgassing requirements. The
contaminants were removed from internal cavities as well
as the external surfaces of the substrate.

30 The general procedure described in Example 1 was
followed except that 100 percent carbon dioxide was used
as the dense phase gas. The phase shift temperature range
was 305K to 325K at about 340 atmospheres. Phase shifting
was carried out at a rate of 1 cycle very 10 minutes.
35 Following cleaning operations, the substrate was

1 thermal-vacuum degassed at 375K and 1 Torr (millimeter of
mercury) for 30 minutes. The cleaned substrate was
packaged and sealed. The cleaned substrate exhibited a
TML of less than 1.0% and a VCM of less than 0.1%.

5 The above-described cleaning operation utilizing dense
phase carbon dioxide can be extended to other types of
substrates containing a wide range of contaminants
including spacecraft fasteners, linear bearings, and heat
pipes.

10

EXAMPLE 6

This example illustrates the use of the process of the
present invention to remove non-aqueous and semi-aqueous
15 photoresist from printed wiring boards in order to prepare
the boards for subsequent processing steps.

The general procedure described in Example 1 was
followed except that the dense phase gas comprised xenon.
Xenon has a critical pressure of approximately
20 57 atmospheres and a critical temperature of approximately
290K. Dense phase xenon was used at approximately
140 atmospheres and a phase shift temperature range of
285K to 300K was used to penetrate, swell, and separate
the photoresist from the substrate. The phase shifting
25 process was carried out as many times as necessary to
effect adequate separation of the photoresist from the
substrate. Optionally, other gases, for example ammonia,
may be added to xenon to produce appropriate blends for
various types of photoresists with varying cohesive
30 energies and properties.

Thus, from the previous examples, it may be seen that
the present invention provides an effective method for
removing two or more contaminants from a given substrate
in a single process. The types of contaminants removed in
35 accordance with the present invention may have a wide

1 variety of compositions and the substrates may vary widely
in chemical composition and physical configuration.

5 The process of the present invention has wide
application to the preparation of structures and materials
for both terrestrial and space environments including
gaskets, insulators, cables, metal castings, heat pipes,
bearings and rivets. The particular cleaning fluid and
phase shifting conditions utilized will vary depending
upon the particular contaminants desired to be removed.
10 The process is also especially well-suited for removing
greases and oils from both internal and external surfaces
of complex hardware.

15 Having thus described exemplary embodiments of the
present invention, it should be noted by those skilled in
the art that the within disclosures are exemplary only and
that various other alternatives, adaptations, and
modifications may be made within the scope of the present
invention. Accordingly, the present invention is not
limited to the specific embodiments as illustrated herein,
20 but is only limited by the following claims.

CLAIMSWhat is Claimed is:

- 1 1. A process for removing two or more contaminants
from a chosen substrate comprising the steps of:
 - a) placing said substrate containing said
contaminants in a cleaning vessel;
 - 5 b) contacting said substrate containing said
contaminants with a chosen dense phase gas at a pressure
equal to or above the critical pressure of said dense
phase gas; and
 - 10 c) shifting the phase of said dense phase gas between
the liquid state and the supercritical state by varying
the temperature of said dense phase gas in a series of
steps between a temperature above the critical temperature
of said dense phase gas and a temperature below said
critical temperature, maintaining said temperature at the
15 completion of each said step for a predetermined period of
time, and maintaining contact between said dense phase gas
and said substrate containing said contaminants for said
predetermined period of time at each said step wherein a
solvent spectrum of said dense phase gas is provided to
20 thereby remove said two or more contaminants from said
substrate.
- 1 2. The process as set forth in Claim 1 wherein said
varying said temperature comprises starting at a first
temperature below said critical temperature, increasing
said temperature to a second temperature above said
5 critical temperature, and then decreasing said temperature
to said first temperature.
- 1 3. The process as set forth in Claim 1 wherein said
varying said temperature comprises starting at a first

temperature above said critical temperature, decreasing said temperature to a second temperature below said critical temperature, and then increasing said temperature to said first temperature.

1 4. The process as set forth in Claim 2 or 3 wherein said varying is performed more than one time.

1 5. The process as set forth in Claim 1 wherein said temperature is varied above said critical temperature by about 5 to 100K.

1 6. The process as set forth in Claim 1 wherein said temperature is varied below said critical temperature by about 5 to 25K.

1 7. The process as set forth in Claim 5 or 6 wherein each said step comprises a change in temperature of about 5 to 10K.

1 8. The process as set forth in Claim 5 or 6 wherein said predetermined period of time is within the range of about 5 to 30 minutes.

1 9. The process as set forth in Claim 1 wherein said dense phase gas is selected from the group consisting of carbon dioxide, nitrous oxide, ammonia, helium, krypton, argon, methane, ethane, propane, butane, pentane, hexane, ethylene, propylene, tetrafluoromethane, chlorodifluoromethane, sulfur hexafluoride, perfluoropropane, and mixtures thereof.

1 10. The process as set forth in Claim 9 wherein said dense phase gas is selected from the group consisting of a mixture of carbon dioxide and nitrous oxide and a mixture of dry carbon dioxide and anhydrous ammonia.

1 11. The process as set forth in Claim 1 wherein said
contaminant is select d form the group consisting of oil,
grease, lubricant, solder flux residue, photoresist,
adhesive residue, plasticizer, unreacted monomer,
5 inorganic particulates, and organic particulates.

1 12. The process as set forth in Claim 1 wherein said
dense phase gas containing said contaminants is
continually removed from said cleaning vessel and replaced
with additional dense phase gas in an amount sufficient to
5 maintain the pressure in said cleaning vessel at or above
said critical pressure.

1 13. The process as set forth in Claim 1 further
including after step "c", subjecting said substrate to
thermal vacuum degassing to thereby remove residual dense
phase gas from said substrate.

1 14. The process as set forth in Claim 1 further
including after step "c", displacing said dense phase gas
with a chosen gas having a relatively high diffusion rate
and then depressurizing said cleaning vessel.

1 15. The process as set forth in Claim 1 wherein said
substrate is suspended in a liquid solvent to thereby
enhance removal of said contaminants from said substrate.

1 16. The process as set forth in Claim 1 wherein said
dense phase gas is exposed to ultraviolet radiation to
thereby enhance removal of said contaminants from said
substrate.

1 17. The process as set forth in Claim 1 wherein said
dense phase gas and said substrate containing said
contaminants are exposed to ultrasonic energy to thereby
enhance removal of said contaminants from said substrate.

1 18. The process as set forth in Claim 1 wherein said
dense phase gas and said substrate containing said
contaminants are exposed to ultraviolet radiation and
5 ultrasonic energy to thereby enhance removal of said
contaminants from said substrate.

1 19. The process as set forth in Claim 1 wherein said
dense phase gas comprises a mixture of a first dense phase
gas capable of chemically reacting with said contaminants
to thereby enhance the removal of said contaminants, and a
5 second dense phase gas as a carrier for said first dense
phase gas.

1 20. The process as set forth in Claim 19 wherein said
first dense phase gas comprises ozone.

1 21. The process as set forth in Claim 20 wherein said
ozone is generated in situ when said dense phase gas is
contacted with said substrate.

1 22. The process as set forth in Claim 1 wherein said
shifting of said phase of said dense phase gas is
accomplished under computer control.

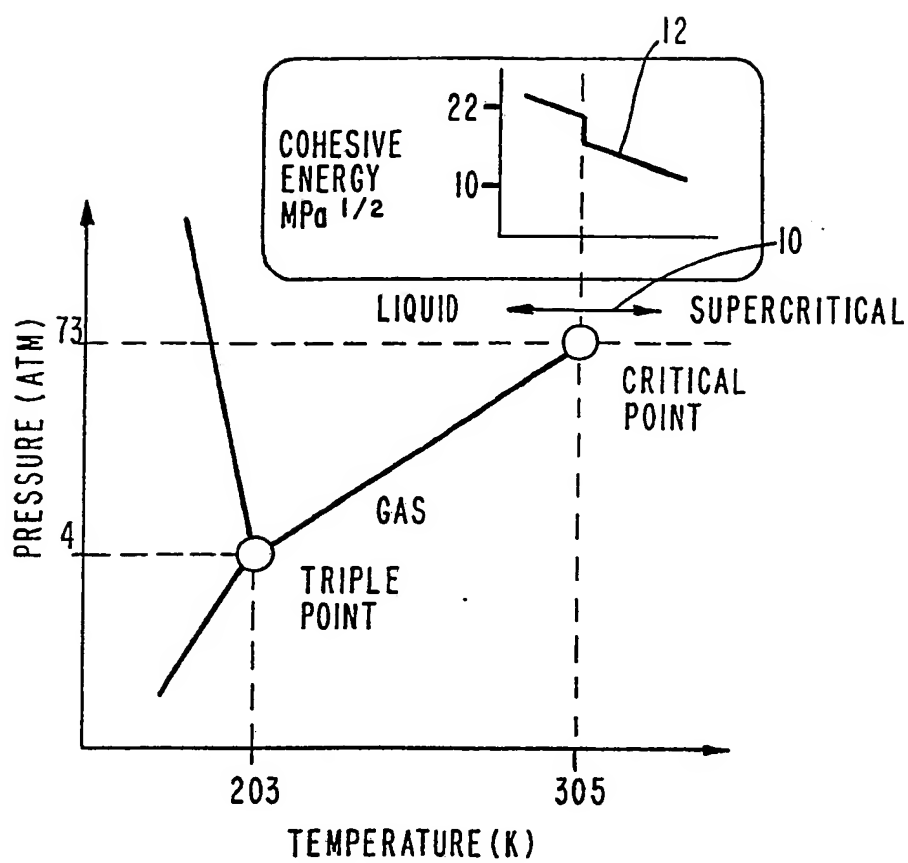


Fig. 1.

Fig. 2.

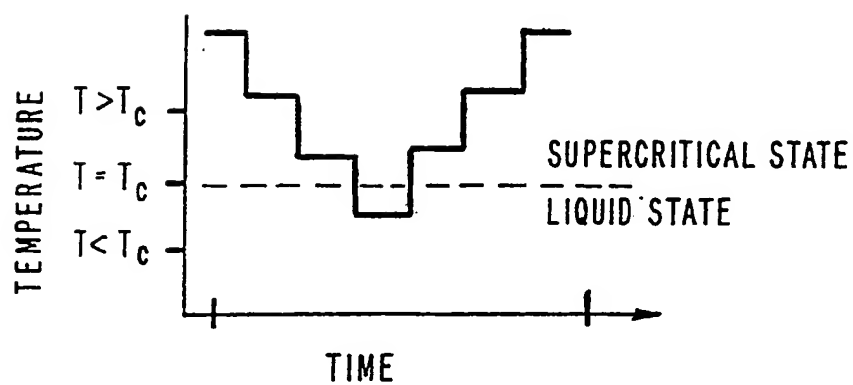
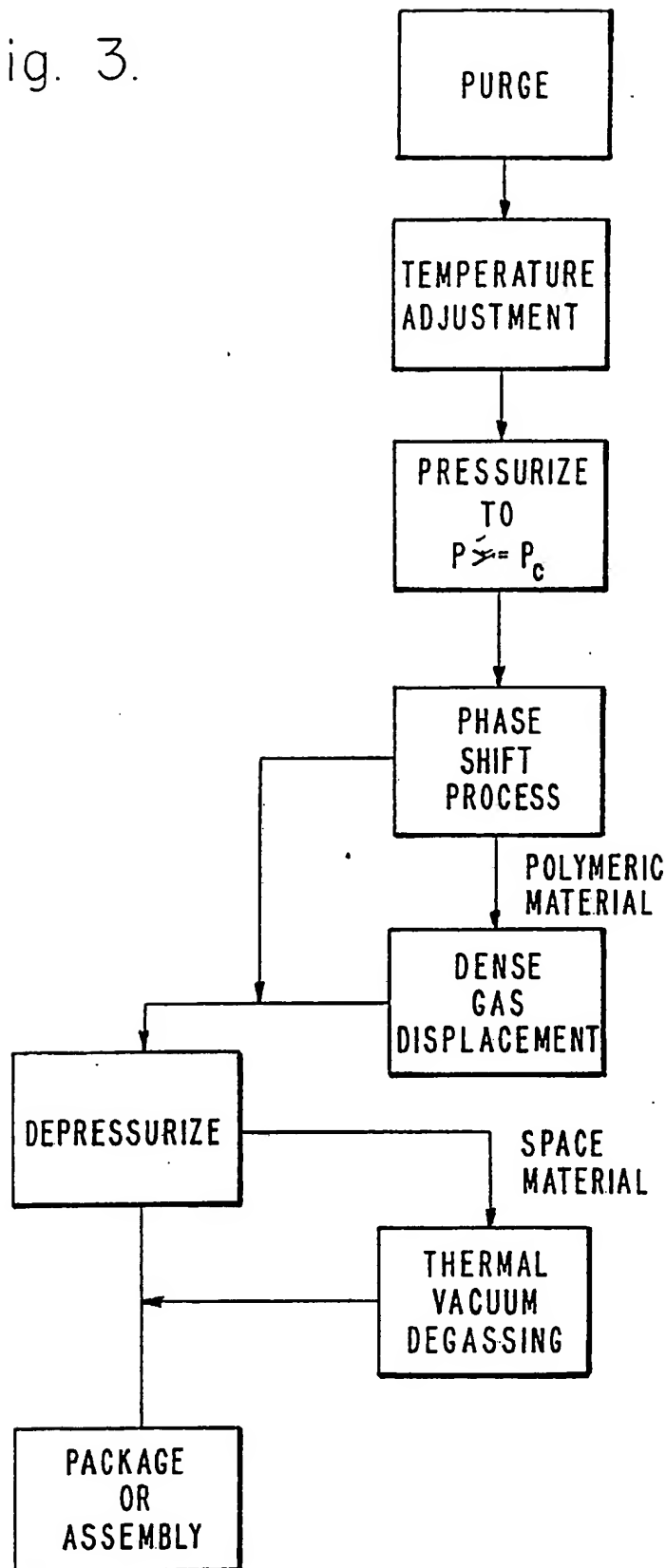


Fig. 3.



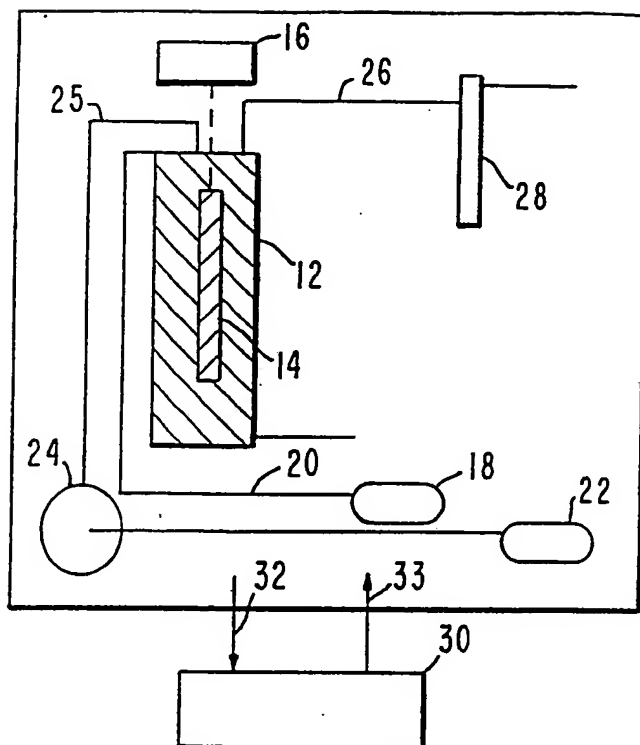


Fig. 4.

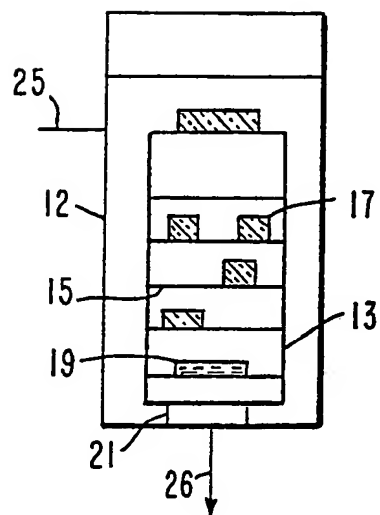


Fig. 5a.

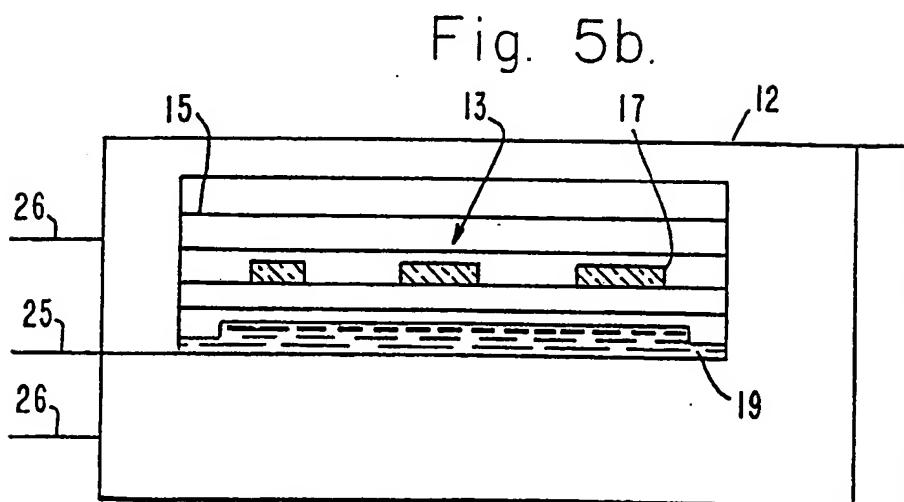


Fig. 5b.

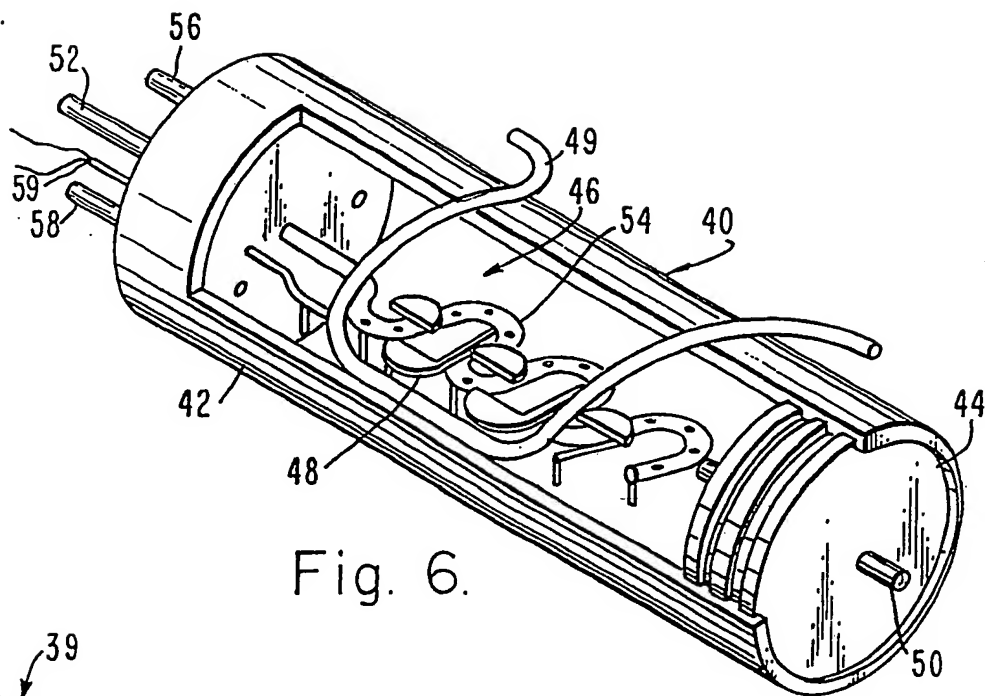


Fig. 6.

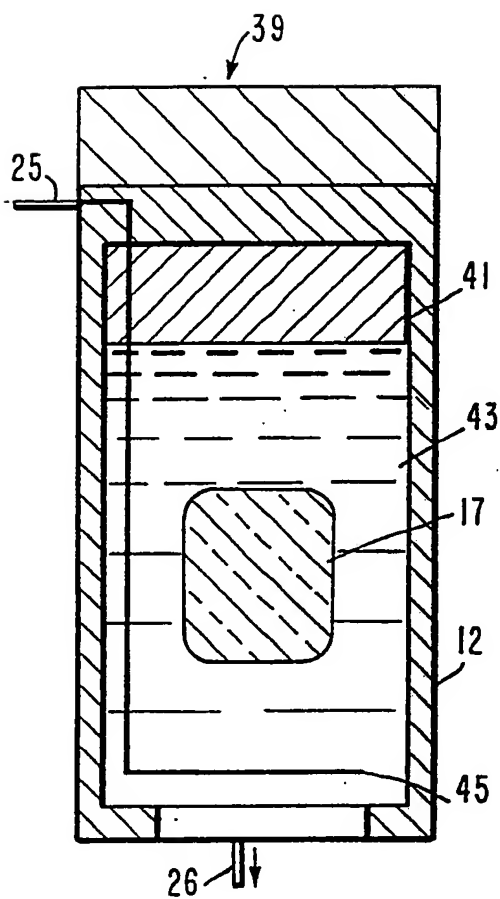


Fig. 7

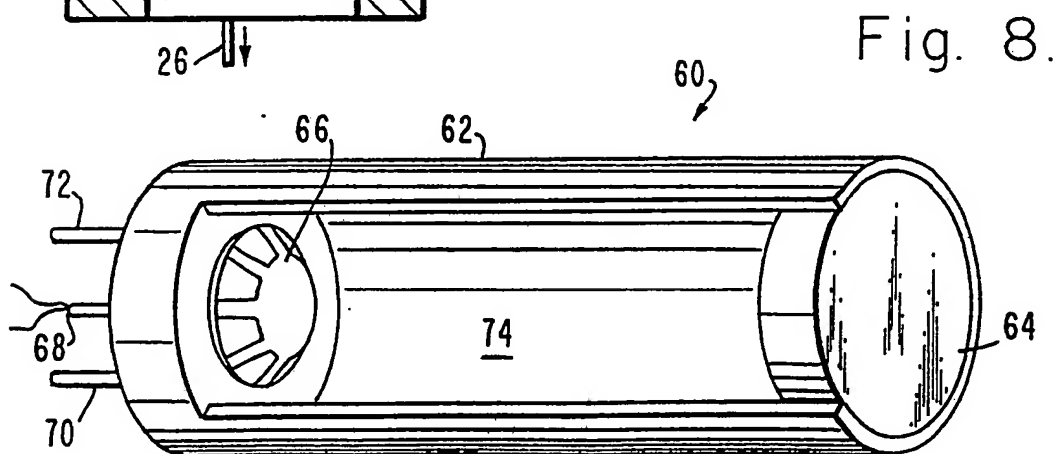


Fig. 8.

Fig. 9a.

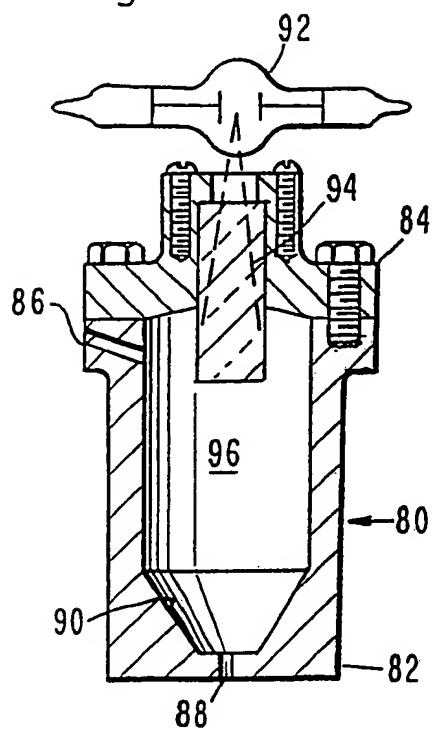
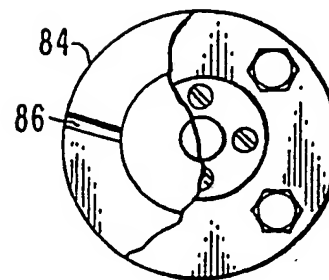


Fig. 9b



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/04674

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: B 08 B 7/00, C 23 G 5/00

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System

Classification Symbols

IPC⁵ : B 08 B 7/00, C 23 G 5/00

Documentation Searched other than Minimum Documentation
to the extent that such Documents are included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

| Category ⁹ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
|-----------------------|--|-------------------------------------|
| A | WO, A, 8402291 (HUGHES AIRCRAFT COMPANY) 21 June 1984 see claims -- | 1 |
| A | Patents Abstracts of Japan, volume 10, no. 35 (E-380)(2092), 12 February 1986 & JP, A, 60192333 (HITACHI SEISAKUSHO K.K.) 30 September 1985 see the abstract -- | 1 |
| A | US, A, 4576837 (G. TARANCON) 18 March 1986 -- | |
| A | DE, A, 2544116 (A.D. LITTLE) 8 April 1976 & US, A, 4124528 cited in the application ----- | |

* Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention.

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

12th April 1990

Date of Mailing of this International Search Report

22.05.90

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

W. P. S.

M. Perez

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 8904674

SA 32339

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 14/05/90
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| WO-A- 8402291 | 21-06-84 | EP-A- 0127643 | 12-12-84 |
| US-A- 4576837 | 18-03-86 | None | |
| DE-A- 2544116 | 08-04-76 | US-A- 4124528 | 07-11-78 |
| | | CA-A- 1064891 | 23-10-79 |
| | | GB-A- 1522352 | 23-08-78 |
| | | JP-A, B, C51061484 | 28-05-76 |
| | | US-A- 4061566 | 06-12-77 |